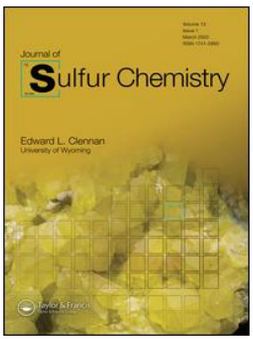

Journal of Sulfur Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gsrp20

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To cite this article: Shuai Huang, Hao Wang, Yongguo Liu, Baoguo Sun, Hongyu Tian & Sen Liang (2021): A novel practical preparation of methyl methanethiosulfonate from dimethyl sulfoxide initiated by a catalytic amount of $(COCl)_2$ or anhydrous HCl, Journal of Sulfur Chemistry, DOI: 10.1080/17415993.2021.1932887

To link to this article: https://doi.org/10.1080/17415993.2021.1932887

JOURNAL OF SULFUR CHEMISTRY
https://doi.org/10.1080/17415993.2021.1932887

A novel practical preparation of methyl methanethiosulfonate from dimethyl sulfoxide initiated by a catalytic amount of $(COCl)_2$ or anhydrous HCl

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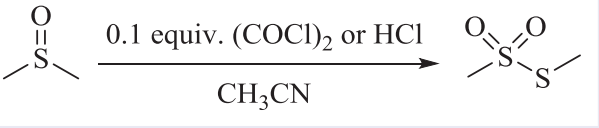
ABSTRACT

A novel practical preparation method for methyl methanethiosulfonate (MMTS) has been developed. Dimethyl sulfoxide was converted to MMTS in the presence of a catalytic amount of oxalyl chloride or anhydrous HCl in acetonitrile under reflux in an ideal yield. Methanesulfenic acid was proposed to be the key intermediate for the formation of MMTS.



ARTICLE HISTORY
Received 13 April 2021
Accepted 16 May 2021

KEYWORDS
Methyl methanethiosulfonate; dimethyl sulfoxide; oxalyl chloride; methanesulfenic acid; methoxydimethylsulfonium salt

Introduction

Thiosulfonates, which are very useful sulfenylating or sulfonylating reagents in organic synthesis, have attracted much attention among the organic community during recent years [1]. In this compound class, methyl methanethiosulfonate (MMTS) is one of the most widely employed thiosulfonates. It is commonly used as a sulfenylating reagent, more reactive than the commonly utilized dimethyl disulfide, and more stable than the highly reactive methanesulfenyl chloride [2]. It is broadly applied in the methylsulfenylation of mercapto groups in enzymes and other biologically active compounds [3–6]. Moreover, a variety of sulfenylated intermediates in organic syntheses can be prepared with MMTS. Substrates with acidic protons, such as 1,3-dicarbonyl compounds [7,8] or lactones [9], can be methylsulfenylated with MMTS after deprotonation in the presence of a base. It can also serve as a protective reagent for amino groups [10]. A methylthio group can be introduced into different heterocycles with MMTS via metalation [11–13]. It can be used to convert 1-alkenylalumiunum derivatives into sulfides efficiently [14]. In addition, MMTS was reported to exist in various vegetables, such as broccoli [15], mushroom [16], cabbage

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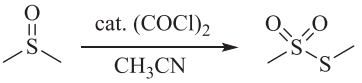


Scheme 1. Preparation of MMTS from DMSO with a catalytic amount of $(COCl)_2$.

[17,18] and cauliflower [19], which was claimed to possess antibacterial activity [17,18] and antimutagenic activity [19].

Some strategies for thiosulfonate synthesis have been developed due to increasing interest in this class of compounds, which can be prepared from various chemical feedstocks, such as disulfides, thiosulfinates, thiols, sulfenyl halides, sulfonyl halides, alkali metal thiosulfonates or sulfinates, or sulfonyl hydrazides [1]. To the best of our knowledge, no economically attractive synthetic methods have been described for methyl methanesulfonate. Traditional preparation methods of MMTS include hydrolysis of methanesulfenyl chloride made by oxidation of dimethyl disulfide with chlorine [20,21], silver-assisted displacement on sulfur of disulfide with sodium methanesulfinate [22], reduction of sulfonyl halides with potassium iodide [23] or activated zinc powder [24–27], or oxidation of dimethyl disulfide with microwave-supported permanganate or hydrogen peroxide in AcOH [28,29]. In addition, Laszlo and Mathy accidentally discovered that dimethyl sulfoxide (DMSO) can be converted into MMTS by treatment with chlorotrimethylsilane and ethylene glycol [30].

DMSO is a versatile source for various synthons including methyl, methylene, methine, methylthio, methylthiomethyl, methyl sulfinyl, methylsulfinylmethyl etc [31–33]. Our recent work has focused on the application of combination reagents containing sulfoxide and oxalyl halide [34] in various chemical transformations, including sulfenyllactonization [34] or chlorolactonization [35] of alkenoic acids, bromination [36], sulfenylchlorination [37] or oxysulfenylation [38] of alkenes, dehydration of primary amides or aldoximes [39], sulfenyletherification of alkenols [40], and the preparation of unsaturated lactones from 3-alkenoic acids [41,42]. During the investigation of alkene oxysulfenylation with DMSO/$(COCl)_2$ [38], we fortuitously discovered that MMTS can be obtained cleanly from DMSO with a catalytic amount of $(COCl)_2$ (Scheme 1) [43].

Results and discussion

Originally, methyl methanethiosulfonate was found in our work on the oxysulfenylation of alkenes, which involved treating an alkene with DMSO/$(COCl)_2$ followed by reacting with *p*-cresol in the presence of K_2CO_3 [38] Stimulated by the results, a series of experiments were conducted to investigate its formation in this reaction system. Several control experiments were carried out by modifying the conditions in oxysulfenylation of alkenes without the addition of alkene and *p*-cresol [38]. MMTS produced in the reaction mixture was analyzed semiquantitatively by GC/MS with an internal standard (Table 1).

The typical procedure is as follows: to a solution of dimethylsulfoxide (DMSO, 30 mmol, 2 equivalents) in acetonitrile cooled at 0°C was added dropwise a solution of oxalyl chloride (15 mmol, 1 equivalent) in acetonitrile. Then K_2CO_3 (2 equivalents) was added and the reaction mixture was allowed to warm to room temperature and then heated to reflux. The reaction was shown to be complete after refluxing for 2 h by GC/MS analysis. The

Table 1. Investigation on the conditions for the formation of MMTS.

Entry	Reagents (equiv.)	Conditions	Yield (%)[a]
1	DMSO/$(COCl)_2$/K_2CO_3(2/1/2)	CH_3CN, 0°C-reflux, 2 h	9
2	DMSO/K_2CO_3(1/1)	CH_3CN, 0°C-reflux, 8 h	0
3	DMSO/$(COCl)_2$(2/1)	CH_3CN, 0°C-reflux, 2 h	8
4	DMSO/$(COCl)_2$(3/1)	CH_3CN, 0°C-reflux, 2.5 h	10
5	DMSO/$(COCl)_2$(3/1)	CH_2Cl_2, 0°C-reflux, 8 h	5
6	DMSO/$(COCl)_2$(10/1)	CH_3CN, 0°C-reflux, 3.5 h	19
7	DMSO/$(COCl)_2$(20/1)	CH_3CN, 0°C-reflux, 6 h	19
8	DMSO/$(COCl)_2$(30/1)	CH_3CN, 0°C-reflux, 10.5 h	19

[a]GC yields. The amount of MMTS in the reaction mixture was determined using *n*-pentyl acetate as an internal standard via GC/MS. The yields were calculated based the amount of MMTS formed from one equivalent of DMSO.

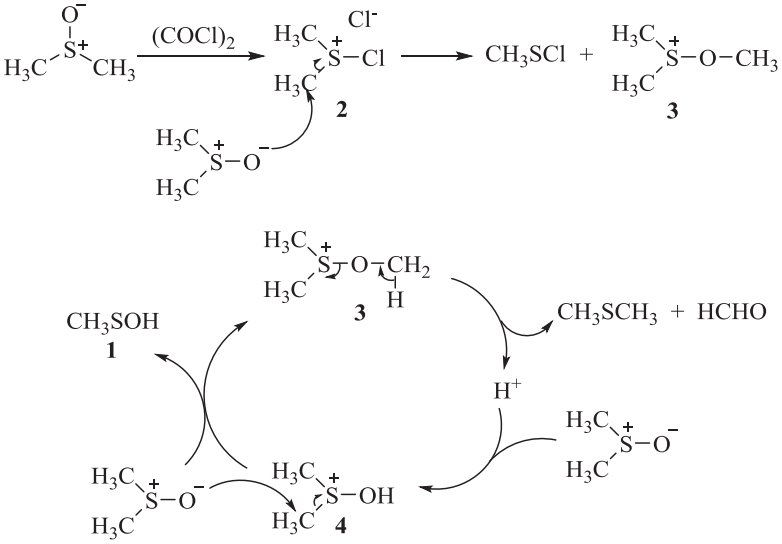
content of MMTS in the reaction mixture was determined by the internal standard method. The yield was about 9% based on the amount of DMSO (entry 1). An experiment was carried out in the absence of $(COCl)_2$ with the other conditions the same as those in entry 1. GC/MS analysis showed that DMSO was unchanged without MMTS formed after refluxing for 8 h (entry 2). The reaction of DMSO with $(COCl)_2$ also produced MMTS in about 8% yield in the absence of K_2CO_3 with the other conditions the same as those in entry 1 (entry 3). The following reaction was carried out with an increased ratio of DMSO/$(COCl)_2$ 3/1 and the yield of MMTS increased slightly to 10% (entry 4). Whereas when the reaction was carried out in CH_2Cl_2, about half of DMSO remained after refluxing for 8 h with a 5% yield (entry 5). We observed that no DMSO was left in the reaction of entry 4 even though the amount of DMSO was excess compared with that in the reaction of entry 3. Therefore, we wondered whether stoichiometric amount of $(COCl)_2$ was necessary in this reaction. Subsequently, a reaction was carried out with a DMSO/$(COCl)_2$ ratio of 10/1 and monitored by GC/MS. It was found that DMSO disappeared completely in 3.5 h and the yield of MMTS increased to 19% (entry 6). This result suggested that the formation of MMTS did not require a stoichiometric amount of $(COCl)_2$. The reaction can occur as well when the ratio of DMSO/$(COCl)_2$ increased further to 20/1, affording MMTS in about 19% yield within 6 h (entry 7). Impressively, MMTS was still able to be produced even with a DMSO/$(COCl)_2$ ratio of 30/1. However, the reaction seemed to slow down in that approximately 2/3 of the DMSO remained unreacted after refluxing for 4 h. The reaction was accomplished in 10.5 h with a final yield approaching about 19% (entry 8).

Initially, the formation of MMTS was merely analyzed by GC/MS without separation for calculating yields. Further experiments with different DMSO/$(COCl)_2$ ratios were done on a larger scale with 0.1 mol of DMSO and the products were purified by column chromatography (Table 2). The reaction was complete after refluxing for 2.5 h when the ratio of DMSO/$(COCl)_2$ was 4/1, affording MMTS in 11% yield (entry 1, Table 2). When the amount of $(COCl)_2$ was reduced (DMSO/$(COCl)_2$ = 10/1), the yield of MMTS increased to 16% (entry 2, Table 2). In contrast, the reaction took longer time to complete with a 18% yield when the amount of $(COCl)_2$ was reduced further (DMSO/$(COCl)_2$ = 20/1) (entry 3, Table 2). Considering the time cost, a 10/1 ratio of DMSO/$(COCl)_2$ is more reasonable for the practical production of MMTS. Thus, the preparation of MMTS was performed on a large scale of 1 mol DMSO with a 10/1 ratio of DMSO/$(COCl)_2$ and the product was purified by vacuum distillation with a 16% average yield.

Table 2. Investigation of MMTS formation on a larger scale.

Entry	Reagents (equiv.)	Conditions	Yield (%)[a]
1	DMSO/$(COCl)_2$(4/1)	CH_3CN, 0°C-reflux, 2.5 h	11
2	DMSO/$(COCl)_2$(10/1)	CH_3CN, 0°C-reflux, 3.5 h	16
3	DMSO/$(COCl)_2$(20/1)	CH_3CN, 0°C-reflux, 7 h	18

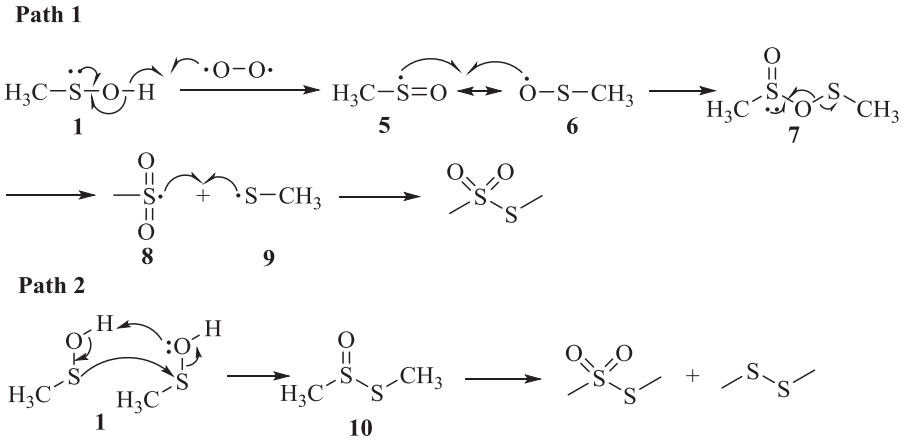
[a]Separation yields based on column chromatography.



Scheme 2. A proposed mechanism for the formation of methanesulfenic acid from DMSO initiated by $(COCl)_2$.

From above results, methanesulfenic acid (**1**) is proposed to be formed initially as the key precursor for MMTS formation (Scheme 2). It is well known that the reaction of DMSO with $(COCl)_2$ rapidly generates chlorodimethylsulfonium salt (**2**) as an intermediate, which is the key active species in Swern oxidation. DMSO attacks the methyl group of chlorodimethylsulfonium salt via nucleophilic substitution leading to the formation of methanesulfenyl chloride and methoxydimethylsulfonium salt (**3**), which was reported by Bellesia *et al* [44] and also observed in our previous work [34]. The methoxydimethylsulfonium salt (**3**) further decomposes to dimethyl sulfide, formaldehyde, and a proton (H^+). The transfer of this proton to DMSO produces hydroxydimethylsulfonium salt (**4**), which is subsequently attacked by DMSO on the methyl group via nucleophilic substitution to regenerate methoxydimethylsulfonium salt (**3**) and release methanesulfenic acid (CH_3SOH, **1**). In our previous work, formaldehyde formed in this regeneration cycle of methoxydimethylsulfonium salt (**3**) was utilized for the preparation of *N*-acylbenzoxazines from phenols and nitriles [45].

Two pathways are proposed for the conversion of methanesulfenic acid (**1**) to MMTS (Scheme 3). The first mechanism involves oxygen as an oxidant, since the reactions were carried out under an air atmosphere. It abstracts a hydrogen atom from methanesulfenic acid (**1**) via homolytic bond cleavage to yield a methylsulfinyl radical (**5**). It can combine with its resonance structure (an *O*-centered radical, **6**) to give labile



Scheme 3. Two possible pathways for the generation of MMTS from methanesulfenic acid (**1**).

OS-methanesulfenyl methanesulfinate (**7**). Subsequently, this unstable intermediate collapses to a methanesulfonyl radical (**8**) and a methanesulfenyl radical (**9**), which can recombine at the sulfur atoms to yield MMTS. In the other pathway, methanesulfenic acid (**1**) undergoes self-condensation to generate methyl methanethiosulfinate (**10**) followed by disproportionation to yield MMTS with dimethyl disulfide. Both pathways can be supported by literature. Sulfenic acids have been taken as the precursors for thiosulfinates and thiosulfonates [46–51], which are very common in the organosulfur chemistry of the genus *Allium* [52–54]. It was reported that *t*-butylsulfenic acid was converted to *S*-*t*-butyl *t*-butanethiosulfonate in the presence of di-*t*-butyl peroxide via a sulfenyl sulfonate [46], which is similar to the first pathway we proposed in Scheme 3. In addition, Pratt et al. established that sulfenic acids have among the weakest O-H bonds known (ca. 70 kcal mol^{-1}) and demonstrate high radical-trapping activity, which accounts for antioxidant activity of extracts of garlic and petiveria [55]. Obviously, this kind of antioxidant activity exploits autoxidation of sulfenic acids involving oxygen. On the other hand, the formation of MMTS from methanesulfenic acid via disproportionation of methyl methanethiosulfinate was reported to occur in garlic [52]. It was also reported methyl methanethiosulfinate (**10**) could be as the precursor of MMTS [56]. In addition, Wen et al. proposed that MMTS derived from DMSO was the possible active species in acid promoted direct cross-coupling of methyl ketones with dimethyl sulfoxide [57].

Which pathway methanesulfenic acid (**1**) would take to produce MMTS in this present work? If the formation of MMTS occurred through the first pathway, four equivalents of DMSO would produce one equivalent of MMTS theoretically; in comparison, the formation of one equivalent of MMTS would require eight equivalents of DMSO by the second pathway. Generally, the separated yield under optimized conditions in our work is about 16%, based on which it was calculated that about six equivalents of DMSO produce one equivalent of MMTS. The average yield we obtained was between the theoretical yields of two possible pathways. The ^{1}H NMR spectrum of the crude product indicated that it is a very clean conversion of DMSO to MMTS. Therefore, we deduce that these two pathways could coexist in the formation of MMTS in our work.

In addition, the presence of dimethyl disulfide can corroborate the second pathway. Indeed, it was detected in the reaction mixture by GC/MS. Moreover, reactions under a nitrogen atmosphere also formed MMTS in similar yields compared to reactions in air. These results implied that the second pathway we proposed does exist. However, apparently the second pathway is not the only mechanism for the formation of MMTS since the amount of dimethyl disulfide observed is much less than MMTS formed in the reaction mixture. Oddly, the amount of dimethyl disulfide did not increase significantly as we expected when the reactions were carried out under a nitrogen atmosphere. This remains elusive and further investigations are required.

The fact that yield of MMTS increases with reduced amount of $(COCl)_2$ can be interpreted reasonably by the mechanism proposed above. The reaction of $(COCl)_2$ with DMSO generates methoxydimethylsulfonium salt (**3**), which decomposes to provide protons as catalyst for the formation of the key active species methanesulfenic acid (**1**). More $(COCl)_2$ would consume more DMSO, which reduces the yield of MMTS. On the other hand, it is logical that a too small amount of $(COCl)_2$ retards the reaction since the amount of protons produced in situ depends on the $(COCl)_2$ loading.

Based upon the aforementioned mechanisms, it appears that DMSO could be converted to MMTS in the presence of a protic acid without needing $(COCl)_2$. Nevertheless, no MMTS was detected when DMSO was treated with 0.1 equivalent of TsOH, CF_3COOH or TfOH after refluxing in CH_3CN for 8 h. Conversely, a trace amount of MMTS was detected after refluxing in CH_3CN for 8 h in the presence of 0.1 equivalent of hydrochloric acid aqueous solution. Moreover, comparable yield of MMTS was obtained when the reaction was carried out in the presence of about 0.1 equivalent of anhydrous hydrogen chloride instead of $(COCl)_2$. These results indicated that a protic acid with enough acidity is necessary for the generation of methanesulfenic acid (**1**). In addition, water has an adverse effect on the reaction since only a trace amount of MMTS was detected when hydrochloric acid aqueous solution was used. Thus, it can be concluded from these results that the mechanisms we proposed are reasonable.

There are two known preparation methods of MMTS involving DMSO. One was reported by Laszlo and Mathy [30], who discovered it accidentally when preparing formaldehyde acetals from alcohols and chlorotrimethylsilane in the presence of DMSO. As pointed out by Maes et al., this method is unpractical in terms of atom economy, reaction mass efficiency, and reaction process mass intensity [1]. The other method was reported by Rätz and Sweeting in which MMTS was obtained as a byproduct without yield given [58]. Evidently, the synthesis of MMTS in this present work is distinct from those reported in the literature. Compared with the existing methods, our method is much more advantageous from the following aspects: (1) Clean conversion under benign experimental conditions within a short reaction time; (2) Low synthetic cost and high reproducibility. In practice, producing 1 equivalent of MMTS requires about 6 equivalents of DMSO and less than 0.6 equivalents of $(COCl)_2$ or HCl. The reactions have been repeated many times with high reproducibility. The reagents are cheap and the solvent can be recycled. Among all the existing methods, it is worth noting that Maddaluno et al. reported that MMTS was obtained in 86% yield by the oxidation of dimethyl disulfide with hydrogen peroxide in AcOH [29]. Although it took 24 h to complete the reaction without large scale data, it looks quite practical. Compared with this method, our method has several advantages, such as short reaction time, catalytic amount of reagent, and recyclable solvent.

In addition, the transformation of methylphenyl sulfoxide to phenyl benzenethiosulfonate was also explored under the above optimized conditions. Unfortunately, only a small amount of phenyl benzenethiosulfonate was detected. This transformation should be achievable according to the mechanisms we proposed. Further study about this transformation and other sulfoxides is currently underway.

Conclusion

In summary, MMTS can be prepared in an ideal yield from DMSO with a catalytic amount of $(COCl)_2$ or anhydrous HCl after simple operations. Possible mechanisms are proposed, in which methanesulfenic acid is generated as the key species which either undergoes radical reactions via *OS*-methanesulfenyl methanesulfinate or intermolecular condensation to produce methyl methanethiosulfinate intermediate to afford MMTS. It is easy to scale up and quite suitable for the industrial production of MMTS. This practical approach has the potential to replace the current preparation method for MMTS in industry.

Experimental

General procedures for preparation of methyl methanethiosulfonate from DMSO and $(COCl)_2$ or anhydrous HCl. To a solution of DMSO (78 g, 1.0 mol, 1 equiv.) in CH_3CN (200 mL) cooled at 0°C was added dropwise a solution of oxalyl chloride (8.7 mL, 0.1 mol, 0.1 equiv.) in CH_3CN (50 mL) under an air atmosphere (DMSO and CH_3CN were used directly without treatment with drying agents). When anhydrous HCl was used, a solution of anhydrous HCl in CH_3CN was prepared as follows. To concentrated H_2SO_4 (30 mL) was added dropwise concentrated HCl. The HCl gas generated passed through a water trap filled with conc. H_2SO_4 and a column of blue silica gel sel, then was bubbled into CH_3CN in a round-bottom flask with a known weight at room temperature. After about 3.6 g of HCl (0.1 equiv.) was absorbed by CH_3CN, DMSO (1 equiv.) was added. The mixture was then allowed to warm up to reflux. The reaction was monitored by GC/MS and was complete in 3.5 h. The mixture was concentrated with a rotary evaporator under reduced pressure. CH_2Cl_2 (100 mL) was added to the residue and washed with saturated aqueous $NaHCO_3$ and brine successively. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuum. Distillation under reduced pressure afforded 20.5 g of MMTS as a colorless oil (16% yield, bp 69–72°C/0.4 mm). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.31 (s, 3 H), 2.70 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.8, 18.3. All measured values were identical to those in the literature [30].

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

Financial support from the National key research and development program [grant numbers 2017YFB0307502, 2016YFD0400801].

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